

PATENT SPECIFICATION

1,077,031

NO DRAWINGS.

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:— HEINRICH KRIMM, of 16, Bodelschwinghstr., Krefeld-Bockum, Germany, and HERMANN SCHNELL, of 15, Franz-Stollwerck-Strasse, Krefeld-Uerdingen, Germany, both of German nationality.

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COMPLETE SPECIFICATION.

A Process for the Production of Isocyanates.

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of isocyanates by reacting primary amines or acid-addition salts thereof with phosgene in the presence of a tertiary amine.

It is known that isocyanates can be prepared by reacting primary amines with excess phosgene, initially at temperatures around room temperature and then at higher temperatures up to the boiling point of the solvent used, generally at temperatures of up to 100 to 200°C., followed by the addition of further quantities of phosgene to the reaction mixture until the reaction is complete. In this second stage of the process, the so-called "hot phosgenation stage", hydrogen chloride is given off and escapes from the reaction mixture together with excess phosgene.

In a modification of this process, the free primary amines are replaced by their salts, mainly the hydrochlorides, which are converted into isocyanates by hot phosgenation in accordance with the second stage of the aforementioned process in a slower reaction, during which the hydrogen chloride that forms is removed.

These known processes have a number of

disadvantages so that they are of limited use.

For example, the evolution of hydrogen chloride creates problems of corrosion. In addition, the quantity in which the phosgene has to be used is generally three to seven times larger than the stoichiometric quantity. Since the excess phosgene escapes with the liberated hydrogen chloride, extensive safety precautions have to be taken, because of the high toxicity of phosgene.

Due to the evolution of hydrogen chloride and to the formation of volatile intermediate products, it is not possible to prepare isocyanates of low boiling point, such as the first members of the aliphatic series. In this instance, the corresponding carbamic acid chlorides are the only, or at least the main, reaction products. The extent to which the process can be used is also limited by the occurrence of undesired secondary reactions initiated by the hydrogen chloride given off at high temperatures, such as the replacement of amine groups by chlorine in the aliphatic group, ether-splitting reactions or polymerisation reactions.

In addition, the use of catalytic quantities of tertiary amines has been proposed to accelerate isocyanate formation, although it was later reported that these catalysts do not afford any real advantages and, in fact, initiate polymerisation of the isocyanates when the reaction mixtures are worked up by distillation.

The process according to the invention obviates the disadvantages attending the pro-

cesses referred to above. The process according to the invention comprises reacting primary amines or their acid-addition salts, optionally in the presence of a solvent, with at least stoichiometric quantities of phosgene and, in spite of what has already been reported, in the presence of a tertiary amine, used in a quantity sufficient to combine with all the hydrogen chloride liberated and with any other acids which are given off.

Surprisingly, the isocyanates are not polymerised during distillation, providing the hydrochlorides of the tertiary amines are removed beforehand by washing with water. In cases where readily volatile isocyanates are formed, there is actually no need to wash out the tertiary amines. In this case, the reaction products may be directly removed from the reaction mixture by distillation.

In addition, the smooth course of the process according to the invention is in itself surprising because tertiary amines are known to react readily with phosgene. For example, aliphatic tertiary amines react with phosgene to form alkyl halides and carbamic acid chlorides of secondary amines, whilst aromatic tertiary amines, dimethyl aniline for example, react with phosgene to form *p*-dimethylamino-benzoyl chloride or dyestuffs.

The process according to the invention not only produces high yields of isocyanates, which are often superior to those obtained by the known phosgenation processes, it also provides high yields of other isocyanates which previously could only be obtained in poor yields by phosgenation or could not be obtained at all. Examples of such isocyanates are aliphatic isocyanates of low molecular weight, such as methyl isocyanate, ethyl isocyanate, propyl isocyanate and allyl isocyanate, as well as ether isocyanates and ester isocyanates which dissociate under the conditions of the previously known phosgenation processes.

Another advantage of the process according to the invention is that the aliphatic isocyanates which are formed are not contaminated by chlorine compounds, because the hydrogen chloride which is liberated is combined by tertiary amines. As a result, there is no need for fractionation, which not only reduces the yields but is also very expensive.

One very important advantage of the process according to the invention is that the actual phosgenation reaction takes very little time. Whereas the known processes generally took from 4 to 20 hours, depending upon the reactivity and solubility of the amine to be reacted, reaction times as short as one to two hours are sufficient to react even sluggishly reacting aromatic amines by the process according to the invention. The small amount of phosgene required is another advantage of the new process.

These advantages are not offset by the expense of the tertiary amines because these can be recovered quantitatively from the aqueous solutions without any difficulty, by precipitation with inorganic bases, such as caustic lime.

Primary amines which are suitable for use in the process according to the invention include, for example, monoamines such as methylamine, ethylamine, propylamine, isopropylamine, butylamine, sec.-butylamine, isobutylamine, tert.-butylamine, n- or isohexylamine, n- or iso-octylamine, dodecylamine, stearylamine, cyclohexylamine, aniline, *o*-, *m*- and *p*-toluidine, *m*- and *p*-xylydine, *o*-, *m*- and *p*-chloro and bromoaniline, 3,4-dichloroaniline, 4-fluoroaniline, 4-trifluoromethyl aniline, *o*-, *m*- and *p*-nitroaniline, mesidine, cumidine, 4-amino-diphenyl, 1- or 2-naphthylamine, benzylamine, 4-chlorobenzylamine and phenylethylamine; as well as diamines such as ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, 1,4-diaminocyclohexane, 4,4'-diaminocyclohexyl methane, 4,4'-diaminodicyclohexyl dimethyl methane, 4,4'-diaminodiphenyl sulphone, *o*-, *m*- and *p*-phenylene diamine, 1-chloro-2,4-diaminobenzene, 2,4-toluylene diamine, 2,6-toluylene diamine or mixtures of these isomers, benzidine, 4,4'-diamino-diphenyl methane, 4,4'-diaminodiphenyl dimethylmethane, 4,4'-diaminodiphenyl - 1,1 - cyclohexane, 4,4'-diaminodiphenyl phenylmethane, 4,4'-diaminodiphenyl phenylmethyl methane, 1,4-xylylene diamine, 1,4-phenylene diisopropylidene diamine, 4-aminophenyl-4'-aminocyclohexyl methane, 1,4-diamine naphthalene, 1,5-diaminonaphthalene and 2,6-diamino naphthalene; triamines such as 2,4,6-triamino toluene, 1,3,7-triamino naphthalene, 2,4,4'-triaminodiphenyl methane, 4,4',4''-triaminotriphenyl methane and 2,4,4'-triaminodiphenyl dimethyl methane; ether amines such as methylamino propyl ether, ethylamino propyl ether, butylamino propyl ether, cyclohexylamino propyl ether, ethylene-bis-aminopropyl ether, 1,4-butylene-bis-amino propyl ether, anisidine, phenetidine, 3,5'-dianisidine and 4,4'-diamino diphenyl ether; ester amines such as aminoethyl acetate, methyl ϵ -aminocaproate and methyl *p*-aminobenzoate; and unsaturated amines such as allylamine and *p*-isopropenyl aniline.

In place of the free amines, it is also possible, as already mentioned, to react their salts, particularly their carbamates of the formula $[RNCOO]^- [RNH_3]^+$ wherein the groups R are identical, with phosgene in the presence, according to the invention, of a tertiary amine, in which case even higher yields are generally obtained. For example, carbon dioxide may be initially introduced

into the solution of the amine until it is saturated. The phosgene is then added to the solution or suspension of the carbamate in an inert solvent, preferably below the reaction temperature, i.e. at temperatures in the range from -20 to $+20^{\circ}\text{C}$. followed by the dropwise addition of the tertiary amine or its solution at the reaction temperature, i.e. at temperatures in the range from $+10$ to $+30^{\circ}\text{C}$. The beginning of the reaction is not only indicated by a rise in the temperature, but also by the evolution of gaseous carbon dioxide.

In cases where other acid-addition salts of the amines are used, for example their hydrochlorides, sulphates or acetates, the quantity of tertiary amine to be added in accordance with the invention must be increased by the amount necessary to neutralise the acid liberated.

Examples of suitable tertiary amines are trimethylamine, triethylamine, tributylamine, *N,N*-dimethylcyclohexylamine, *N,N*-dimethylbenzylamine, pyridine, alkyl pyridines, quinoline, quinaldine and, in particular, *N,N*-dimethyl aniline and *N,N*-diethyl aniline.

Solvents which are suitable for use in the process according to the invention include hydrocarbons such as benzene, toluene, xylene and cumene, chlorinated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene, dichlorobenzene, chlorotoluene, dichlorotoluene and chloronaphthalenes, and esters such as ethyl acetate and butyl acetate.

The process may be readily adapted to the reactivity of the primary amines to be reacted. If the amines react sluggishly, as is the case with aromatic amines, they are preferably added dropwise or introduced into the solution of phosgene in a suitable solvent at temperatures from 0 to 20°C . The tertiary amine is then added at the rate at which the reaction proceeds. By contrast, the more strongly basic aliphatic or cycloaliphatic amines are best added dropwise, together with the tertiary amine, to the phosgene solution at the reaction temperature. The reaction mixture is then, in both instances, preferably heated in order to terminate the reaction.

In general, the quantity in which the phosgene is used is somewhat in excess of the stoichiometric quantity required according to the reaction equation. In most instances, maximum yields are obtainable with an excess of only 5% by weight of the stoichiometric amount. It is only advisable in a few instances, for example when ring closure reactions could take place to form internal ureas, to use a larger excess of phosgene, for example two to a maximum of three times the stoichiometric quantity.

In most instances, an excess of tertiary amine should be avoided because otherwise numerous secondary reactions involving excess phosgene would take place.

The reaction should generally proceed at temperatures from -10 to $+30^{\circ}\text{C}$. as the tertiary amine is being added. Lower temperatures are preferred in the case of reactive primary amines, whilst somewhat higher temperatures are required to react sluggishly-reacting or difficultly soluble primary amines. As already mentioned, the reaction temperature is preferably increased after the tertiary amine has been added, for example up to the boiling point of the solvent used, but generally not beyond 150°C .

On completion of the reaction, the reaction mixture is cooled to 0 to 20°C . and is then shaken with ice water in order to remove the hydrochloride of the tertiary amine. It is remarkable that the isocyanates, which are very sensitive to water, are not affected by this brief treatment with water. If the isocyanates are not very high boiling, they may be separated by distillation, generally under reduced pressure.

The materials obtained by the process according to the invention are valuable intermediate products which can be used in the manufacture of plastics, foams and lacquers.

EXAMPLE 1

250 g. (2.5 mols) of phosgene are introduced into 2 litres of chlorobenzene at 0 to 5°C . to form a solution into which 226 g. (1 mol) of bis-(4-aminophenyl)-dimethyl methane are introduced. A solution of 484 g. (4 mols) of dimethyl aniline in 500 cc. of chlorobenzene is added dropwise over a period of 1 hour at 20°C . The partly crystalline reaction mixture is heated to 100°C . over a period of 15 minutes, during which a homogeneous solution is formed. The temperature is kept at 100°C . for another 15 minutes. Excess phosgene is removed at $50^{\circ}\text{C}/40-20$ Torr. after which the solution is cooled to 0°C . shaken twice with one litre of ice water and dried over sodium sulphate. After the solvent has been removed at 50 Torr. the bis-(4-isocyanatophenyl)-dimethyl methane is distilled at $172-175^{\circ}\text{C}/0.1$ Torr. Yield 246 g. = 95% of theoretical, m.p. $90-91^{\circ}\text{C}$.

EXAMPLE 2

250 g. (2.5 mols) of phosgene are introduced into one litre of chlorobenzene at 0 to 5°C . to form a solution into which 108 g. (1 mol) of finely powdered *p*-phenylene diamine are introduced. A solution of 484 g. (4 mols) of dimethyl aniline in 400 cc. of chlorobenzene is added dropwise while stirring at 25 to 30°C . over a period of two hours. The solution is heated to 128°C .

over a period of two hours and is then left to cool to 0°C. It is then shaken with ice water and dried over sodium sulphate. The solvent is distilled off at 50 Torr. The reaction product, *p*-phenylene diisocyanate, distils over at 105°C./8 Torr. in the form of a colourless mass which solidifies in crystalline form. Yield 135 g. (84.5% of theoretical), m.p. 95–96°C.

10 EXAMPLE 3

125 g. (1.25 mols) of phosgene are introduced into 300 cc. of benzene at 5°C. to form a solution to which a solution of 99 g. (1 mol) of cyclohexylamine and 242 g. (2 mols) of dimethyl aniline in 200 cc. of benzene is added dropwise while stirring at 20°C. The partly crystalline mixture is then heated to the temperature at which it boils, and is kept at this temperature for one hour. The now homogeneous solution is cooled to 0°C., shaken with 500 cc. of ice water and dried over sodium sulphate. The solvent is removed through a small column, and the cyclohexyl isocyanate is distilled at 55 to 60°C./8 Torr. Yield 105 g. (84% of theoretical).

EXAMPLE 4

150 g. (1.5 mols) of phosgene are introduced into 400 cc. of dichlorobenzene at 5°C. A solution of 45 g. (1 mol) of ethylamine in 200 cc. of dichlorobenzene and 243 g. (2 mols) of dimethylaniline, is then added dropwise at –5 to 0°C. over a period of one hour. The reaction mixture is heated to 80°C. over a period of 10 minutes, and a mixture consisting of phosgene and ethyl isocyanate is slowly distilled off at 45 to 65°C. The ethyl isocyanate is obtained in the form of a colourless liquid by fractional distillation through a column at 56 to 61°C. Yield 46 g. (65% of theoretical).

EXAMPLE 5

250 g. (2.5 mols) of phosgene are introduced into 500 cc. of chlorobenzene at 5°C. to form a solution to which a solution of 116 g. of (1 mol) hexamethylene diamine and 484 g. (4 mols) of dimethyl aniline in 300 cc. of chlorobenzene, is added dropwise with vigorous stirring at 20 to 30°C. over a period of thirty minutes. The reaction mixture is heated to 130°C. over a period of 25 minutes and is kept at this temperature for half an hour. It is then left to cool, after which the excess phosgene is removed at 50°C./40 to 20 Torr. The mixture is then cooled to 0°C. and is shaken with 1 litre of water. The chlorobenzene solution is dried over sodium sulphate and the solvent is removed at 20 Torr. The hexamethylene diisocyanate is distilled at 96 to 110°C./0.3 Torr. Yield 132 g. (79% of theoretical).

EXAMPLE 6

125 g. (1.25 mols) of phosgene are introduced into 300 cc. of chlorobenzene at 5°C. to form a solution to which a mixture of 102 g. (0.5 mol) of 1,4 - butylene - bis - amino-propyl ether, 242 g. (2 mols) of dimethyl aniline and 150 cc. of chlorobenzene is added dropwise while stirring at 20°C. over a period of one hour. The mixture is then heated for another hour at 100°C. and is kept at this temperature for one hour. After cooling to 0°C., the reaction mixture is shaken twice with ice water, and is then dried over sodium sulphate. The solvent is distilled off at 20 Torr. The 1,4-butylene-bis-isocyanato isopropyl ether is distilled after some brief first runnings at 108 to 110°C./0.06 Torr. Yield 90 g. (70% of theoretical).

EXAMPLE 7

125 g. (1.25 mols) of phosgene are introduced into 400 cc. of chlorobenzene at 5°C. to form a solution to which a solution of 127.5 g. (1 mol) of *p*-chloroaniline in 300 cc. of chlorobenzene is added dropwise with rapid stirring at –3 to 0°C. over a period of thirty minutes. A mixture of 306 g. of *N*-methyldecahydroquinoline with the same quantity of chlorobenzene is added over a period of 45 minutes at 20°C., after which the temperature is raised to 80°C. over a period of 10 minutes. The mixture is then cooled to 0°C. and is shaken with ice water. A small amount of a precipitated secondary product is removed by suction-filtering, the layers are separated and the solution of the reaction product, is dried over sodium sulphate and distilled through a column. After removal of the chlorobenzene at 30 Torr. the *p*-chlorophenylisocyanate distils over at 74 to 75°C./8 Torr. in the form of a colourless liquid which solidifies in crystalline form when cooled with ice water. Yield 128 g. (83% of theoretical) m.p. 31–32°C.

EXAMPLE 8

125 g. (1.25 mols) of phosgene are introduced into 1 litre of chlorobenzene at 0°C. to form a solution into which 79 g. (0.5 mols) of 2,7-diamine naphthalene are introduced. A solution of 258 g. (2 mols) of quinoline in 500 cc. of chlorobenzene is then added dropwise over a period of three hours at 20 to 25°C. The mixture is slowly heated to a temperature of 80°C. at which it is kept for one hour. It is then cooled, after which the resulting crystal mass consisting of quinoline hydrochloride and 2,7-naphthylene diisocyanate is suction-filtered. After washing with chlorobenzene, the quinoline hydrochloride is dissolved with ice water, and the reaction product is suction-filtered. It is washed with water and dried in a vacuum drying cabinet. Yield 89 g. (85% of theoretical) of naphthylene-2,7-diisocyanate, b.p.

190—195°C./12 Torr. m.p. 150—152°C. (from chlorobenzene).

EXAMPLE 9

180 g. (1.8 mols) of phosgene are introduced into two litres of chlorobenzene at 0°C. to form a solution into which 120.5 g. (0.5 mol) of 2,2 - (2,4,4' - triaminodiphenyl)-propane are introduced. A solution of 420 g. (3 mols) of quinaldine in 1 litre of chlorobenzene is added dropwise over a period of 30 minutes at 20 to 25°C. The mixture is slowly heated to a temperature of 100°C. at which it is kept for one hour. It is then cooled to room temperature. The crystal mass consisting of quinaldine hydrochloride is suction-filtered, washed with chlorobenzene and the filtrate is cooled to 0°C. It is washed once with ice water and dried over sodium sulphate. The clear solution is then distilled. After removal of the solvent, the isopropylidene-diphenyl-2,4,4' - triisocyanate (isopropylidene - 2,4,4' - triisocyanatodibenzene) distils over at 165 to 168°C./0.7 Torr. in the form of a yellowish liquid. Yield 143.5 g. (90% of the theoretical).

EXAMPLE 10

53 g. (0.53 mol) of phosgene are introduced into 1 litre of chlorobenzene at 5°C. to form a solution into which 54 g. (0.25 mol) of 4,4' - diaminodiphenyl sulphide are introduced. A solution of 121 g. (1 mol) of dimethyl aniline is an equivalent quantity of chlorobenzene is then added dropwise while cooling over a period of 20 minutes at 20 to 25°C. The mixture is heated to 125°C. over a period of 10 minutes and is then cooled to 0°C. After washing twice with ice water, drying over sodium sulphate and removal of the solvent, the diphenylsulphide-4,4' - diisocyanate distils over at 165—168°C./0.15 Torr. in the form of a liquid which solidifies. M.p. 104—105°C., yield 55 g. (81.5% of theoretical).

EXAMPLE 11

116 g. (1 mol) of hexamethylene diamine are dissolved in 800 cc. of chlorobenzene to form a solution which is then saturated with carbon dioxide. It is cooled to 0°C. after which 250 g. (2.5 mols) of phosgene are introduced. A solution of 484 g. of dimethyl aniline in 200 cc. of chlorobenzene is added dropwise to this solution, in which the crystallised carbamate of the hexamethylene diamine is suspended, over a period of 1½ hours at 20°C. The mixture is heated over a period of 30 minutes to a temperature of 100°C. at which it is kept for another 30

minutes and then cooled to 0°C. The reaction mixture is washed twice with ice water and is then dried over sodium sulphate. The solvent is distilled off through a small column at 30 Torr. The hexamethylene diisocyanate distils over at 80 to 85°C./0.05 Torr. Yield 146 g. (87% of theoretical).

WHAT WE CLAIM IS:—

1. A process for the preparation of isocyanates which comprises reacting a primary amine or an acid-addition salt thereof with at least a stoichiometric quantity of phosgene in the presence of a quantity of a tertiary amine sufficient to combine with the hydrogen chloride formed during the reaction and with any other acid which may be liberated.
2. A process as claimed in claim 1 wherein the reaction between the primary amine and acid-addition salt thereof and phosgene takes place in an inert organic solvent.
3. A process as claimed in claim 2 wherein a primary amine or acid-addition salt thereof is added to a solution of phosgene in an organic solvent at a temperature from 0 to 20°C. the tertiary amine is added at a temperature of -10 to +30°C., heating the resulting mixture, washing with ice water and recovering the isocyanate formed.
4. A process as claimed in any of claims 1 to 3 wherein the tertiary amine is trimethylamine, triethylamine, tributylamine, N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine, pyridine, an alkyl pyridine, quinoline, N-methyldecahydroquinoline, quinaldine, N,N-dimethyl aniline or N,N-diethyl aniline.
5. A process as claimed in claim 2 wherein the inert organic solvent is an aromatic hydrocarbon, a chlorinated hydrocarbon or an ester of acetic acid.
6. A process as claimed in any of claims 1 to 5 wherein the primary amine is bis-(4-aminophenyl)dimethyl methane; *p*-phenylene diamine; cyclohexylamine; ethylamine; hexamethylene diamine; 1,4-butylene-bis-aminopropyl ether; *p*-chloroaniline; 2,7-diaminonaphthalene; 2,2 - (2,4,4' - triaminodiphenyl)-propane or 4,4' - diamino-diphenyl sulphide.
7. A process as claimed in any of claims 1 to 6 wherein the primary amine is used in the form of its carbamate, hydrochloride, sulphate or acetate salt.
8. A process as claimed in any of claims 1 to 7 wherein the phosgene is used in an excess of up to 5% by weight of the stoichiometric amount.
9. A process as claimed in claim 1 sub-

stantially as described with reference to any
of the Examples.

10. Isocyanates when produced by a pro-
cess as claimed in any of the preceding
5 claims.

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